Conduction-Electron Spin Resonance in Degenerate Indium Sesquioxide

W. M. Walsh, Jr., J. P. Remeika, and L. W. Rupp, Jr.

Bell Telephone Laboratories, Murray Hill, New Jersey

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Spin resonance due to degenerate conduction electrons has been observed in In_2O_3 crystals grown from flux. The isotropic resonance is characterized by a large, negative g shift ($\delta g \simeq -0.12$) which is markedly strain-sensitive. As a result the CESR line is inhomogeneously broadened, making any interpretation of the line shape quite ambiguous. The spin-lattice relaxation time T_1 appears to be in the range 10^{-5}–10^{-7} sec despite the transport scattering time $\tau \sim 10^{-14}$ sec and the 6% g shift. It is suggested that such behavior may be characteristic of single-valley band edges.

I. INTRODUCTION

A SPIN resonance characteristic of degenerate conduction electrons has been observed in n-type crystals of indium oxide, In_2O_3, in the temperature range between ambient and 1.4°K. The parameters of the resonance spectrum (g value, relaxation time, and line shape) prove to be of physical interest when compared with those of other semiconductors and metals in which conduction-electron spin resonance (CESR) has been detected. In particular we find the spin relaxation time to be remarkably longer than the carrier transport scattering time when the large observed g shift (6%) is taken into account. Following a description of the known properties of the conduction band of indium sesquioxide, the experimental techniques and results are presented (Sec. II). In the next section the rather variable line shapes and widths are discussed, the spin-lattice relaxation time is inferred and the high degree of decoupling between spin and transport scattering is emphasized. A possible causal relation with the single-valley nature of the conduction-band edge is suggested.

Indium oxide is a large-band-gap semiconductor which crystallizes in a complex, body-centered-cubic structure containing sixteen formula units per unit cell. A refined x-ray analysis of the structure has recently been performed by Marezio.[1] Nominally stoichiometric, undoped crystals grown by vapor-phase oxidation of indium metal[2] or by a flux-melt technique[3] are moderately transparent throughout the visible, thin sections having a yellow-green color in transmission. Such crystals prove to be quite highly conducting, however, with σ values in the range of 10 to 100 $(\Omega \text{ cm})^{-1}$. Thermal activation[2] as well as cursory optical absorption experiments[4] suggest a band gap of ~ 3.1 eV. Recently Weiher and Ley[5] have examined the optical properties in detail and deduce the existence of a direct energy gap of 3.75 eV and an indirect (phonon-assisted)

gap of 2.62 eV. It is, therefore, clear that the mobile electrons result from a high density of donor impurities or electron-rich deviations from stoichiometry. Crystals prepared in this laboratory by the flux-melt technique using highly purified chemicals have electron concentrations on the order of 10^{19} cm^{-3}. Spectrographic analysis reveals net impurity contents much too low to account for such a large carrier concentration. An oxygen deficiency (or indium excess) donor mechanism thus appears to be the dominant one in our crystals. Weiher reached the same conclusion concerning his vapor-grown samples which had lower electron concentrations ($n \sim 3 \times 10^{17}$–3×10^{18} cm^3 at room temperature).[2]

Present knowledge of the band structure of indium oxide is imprecise because of low carrier mobility which, presumably, results from the high density of "donor" lattice defects in as-grown crystals.[6] Weiher and his collaborators via a series of transport[2,7] and optical[5] studies have, however, established the following picture of the conduction-band edge: It consists of a single, nearly isotropic valley having an effective mass m^* $\simeq 0.55 m_e$. At the high donor-defect concentrations found in our flux-grown samples the donor states have merged with the conduction band.[2] This leads to near temperature independence of both carrier concentration and mobility. For $n \sim 10^{19}$ cm^{-3}, the degeneracy temperature is $\sim 360°$K ($E_F \sim 31$ meV); therefore, we expect a Fermi distribution of conduction electrons in the temperature range of our experiments (1.4–295°K). The Hall mobility is found to be $\mu \sim 70$ cm^2/V sec which implies a transport scattering time $\tau \sim 2 \times 10^{-14}$ sec, a time comparable to that observed in metals at room temperature. Since conduction-electron spin resonance is observable at room temperature in only the lightest metals (Li, Be, Na, K) where spin-orbit coupling is weakest we might naively expect the spin-lattice re-

[1] M. Marezio, Acta Cryst. **20**, 723 (1966).

[2] R. L. Weiher, J. Appl. Phys. **33**, 2834 (1962).

[3] J. P. Remeika and E. G. Spencer, J. Appl. Phys. **35**, 2803 (1964). The rapid conductivity variation at low temperatures reported in this article is not observed in the purer crystals currently being prepared by the flux technique.

[4] R. E. Dietz (private communication).

[5] R. L. Weiher and R. P. Ley, J. Appl. Phys. **37**, 299 (1966).

[6] Prolonged annealing in an oxygen atmosphere at 1200°C fails to reduce the carrier concentration or appreciably improve the mobility of the flux-grown crystals. It is possible to compensate the material by acceptor doping (Mg) in the melt but the mobility decreases with the carrier concentration ($\mu \sim 1$ cm^2/V sec for $n \sim 10^{14}$ cm^{-3}). Weiher's vapor-grown crystals do, however, exhibit increasing mobility as n decreases due to decreased donor-defect density.

[7] R. L. Weiher and B. G. Dick, Jr., J. Appl. Phys. **35**, 3511 (1964).

laxation time T_1 of In_2O_3 to be much too short to yield a detectable CESR signal. That such pessimism proves unwarranted is both unusual and interesting.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

The magnetic-resonance experiments have been performed near 12 Gc/sec using a standard reflection spectrometer with homodyne detection. Audio-frequency field modulation and synchronous second detection were used to obtain the field derivative of the samples' surface resistance.

The flux-melt technique[3] produces crystals bounded by {100} faces with linear dimensions from fractions of a millimeter up to ~ 2 cm. The larger crystals are generally imperfect (twinning, inhomogeneous color, macroscopic inclusions of the lead oxide-boron sesquioxide flux). Selected surface areas of such crystals have been examined by mounting them outside a TE_{101} rectangular microwave cavity against a thin iris forming the end wall. At best very weak and broad resonance signals were obtained from the ~ 0.2-cm^2 area thus exposed to the microwave magnetic field.

However, if care is taken to quench the melt at temperatures just below the solution point (1600°K), the modest yield often consists of thin (0.05–0.5 mm) rectangular, single-crystal platelets several millimeters

FIG. 2. Schematic derivative-with-respect-to-magnetic field H of the microwave loss due to conduction-electron spin resonance. The linewidth ΔH is defined as the width at half-height of the positive slope peak. The line asymmetry ratio A/B is that of the maximum positive and negative slope peaks. The line "center" H_0 which yields the g value can be precisely defined only if the line shape can be interpreted theoretically.

to a centimeter on a side. Such crystals are often visually "perfect." They are most advantageously examined, as shown in Fig. 1, by mounting them inside the experimental cavity on a thin dielectric spacer (e.g., 0.01-mm Mylar) using silicone grease as a flexible adhesive. In this configuration[8] the conducting sample acts as a far-off-center conductor of a TEM stripline mode. Though not resonant at the natural frequency of the empty waveguide cavity, this nonorthogonal mode severely distorts the microwave field pattern in the vicinity of the sample with two significant consequences: First, the sample's "filling factor" (cavity loading) is increased with an attendent increase in spectrometer sensitivity. Second, microwave currents flow on both faces of the specimen which can lead to line-shape effects in thin samples (see below).

Using the "hot-quenched" samples in the configuration described above, a single, asymmetric, magnetic-dipole transition is observed at an isotropic g value in the range 1.88–1.89. The exact g value varies slightly from sample to sample and is temperature-dependent. The g value is also slightly ambiguous due to the variable line shapes which will be discussed. Since the line shape resembles that observed in metals we define the linewidth, after Feher and Kip,[9] as the difference in magnetic field ΔH between the half-maximum positive-slope points on the field derivative of the power absorption, dR/dH (Fig. 2). Typically we find $\Delta H \sim 10$ G. Values as small as 2.9 G and as large as 25 G have been
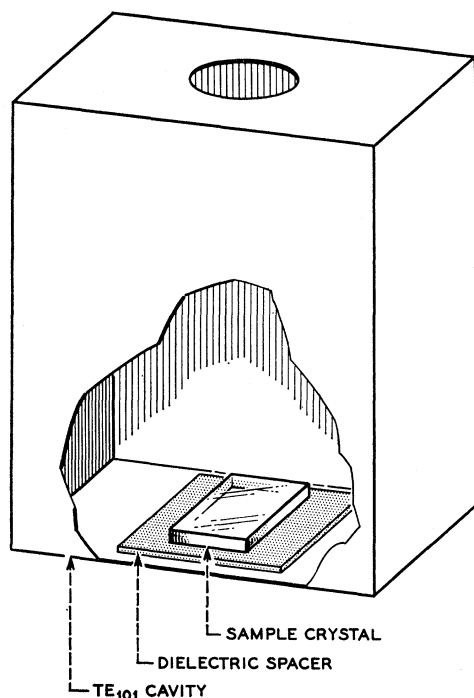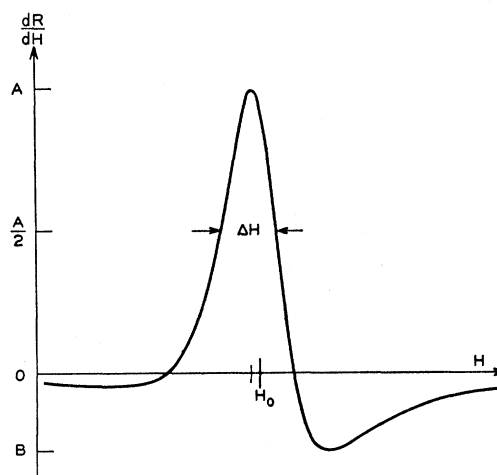

FIG. 1. The experimental arrangement used to examine thin platelet crystals of In_2O_3. The sample is prevented from contacting the cavity end wall by a dielectric layer ~ 0.01 mm thick. This permits the sample to act as one conductor of a TEM stripline mode which, while not resonant at the microwave cavity frequency (~ 11.7 kMc/sec), acts to concentrate the microwave fields in the vicinity of the sample.

[8] This geometry has also proved useful, if not essential, in recent surface-impedance studies of metals: W. M. Walsh, Jr. and P. M. Platzman, Phys. Rev. Letters 15, 784 (1965); W. M. Walsh, Jr., L. W. Rupp, Jr., and P. H. Schmidt, ibid. 16, 181 (1966); Phys. Rev. 142, 414 (1966).

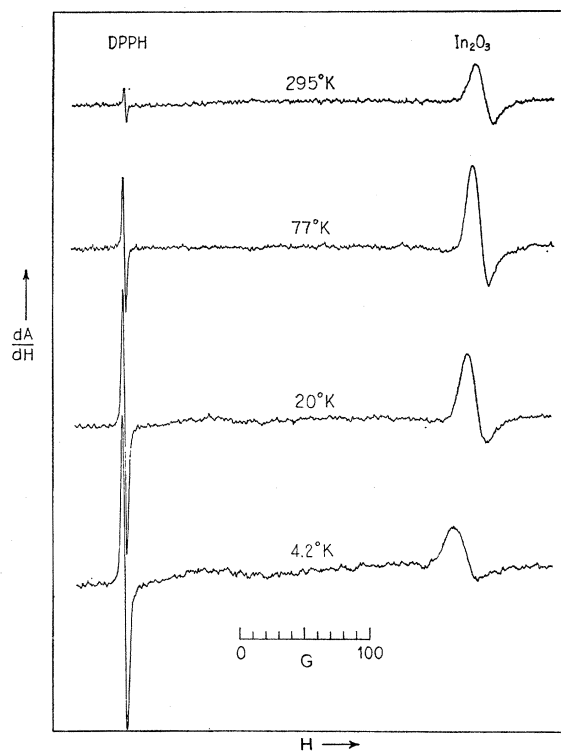[9] G. Feher and A. F. Kip, Phys. Rev. 98, 337 (1955).

FIG. 3. Experimental traces of the differentiated cavity loss versus applied magnetic field H at various temperatures. The signal at the right is the conduction-electron spin resonance of a thin platelet of n-type In_2O_3. That at the left is due to a paramagnetic free radical marker ($\alpha\alpha$-diphenyl-β-picryl hydrazyl $g=2.0036$). The indium sesquioxide signal intensity is approximately temperature-independent whereas the free radical signal intensity increases as the temperature decreases. The latter variation should go as T^{-1} down to $\sim 20°K$ but deviates from the simple Curie law in the liquid-helium range due to incipient spin ordering.

Initially we were disturbed by a few samples which exhibited asymmetry ratios less than the static-spin value (1.4 being the smallest observed value). These samples were particularly thin (0.05 to 0.1 mm thick) and were, in fact, essentially "transparent" since the microwave skin depth δ at frequency ν is

$$\delta = (c/2\pi)(\sigma\nu)^{-1/2} \sim 0.04 \text{ mm}$$

in our material. The excitation on both faces of the sample mentioned above enhances this transparency which would lead to $A/B = 1$ in the limit of a very thin specimen. The use of thicker samples (0.3–1 mm) invariably resulted in asymmetry ratios $\overset{\sim}{>}3$ at room temperature.

The resonance parameters other than intensity of the sample exhibiting the narrowest line (see Fig. 4) behaved as follows as the temperature was varied from 295 to 1.4°K (similar effects may be seen in Fig. 3):

1. The magnitude of the g shift, $\delta g \equiv g - 2.0023$, decreased by $\sim 5\%$ (Fig. 5).
2. The linewidth ΔH decreased slightly, achieved a minimum at 77°K, then broadened by a factor of 3 (Fig. 5).
3. The asymmetry ratio A/B increased from 3.7 to 7.5. The g shift and linewidth variations are qualitatively similar when displayed on suitable scales (Fig. 5). This suggests that the two effects are closely related, i.e., that the g shift is strain sensitive and that the linewidth results from a distribution of g values due to inhomogeneous, "frozen-in" strains. The latter idea was tested by examining a sample at 35 Gc/sec as well as 12 Gc/sec. Because of decreased spectrometer sensitivity at the higher frequency, the CESR was barely
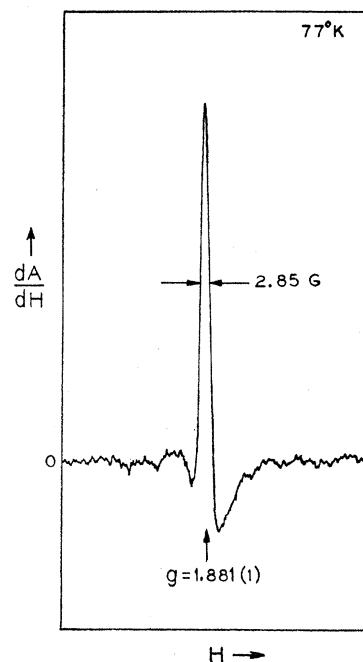
observed in the platelets. The line shape also proves rather variable but generally dR/dH has an asymmetry (ratio of maximum positive to maximum negative slope values, A/B in Fig. 2) of ~ 3 at room temperature, increasing somewhat at lower temperatures. Since the asymmetry ratio is often near the value 2.7 characteristic of *static* spins in a conducting medium thick compared to the microwave skin depth,[10,11] one could suspect the signal to arise from static paramagnetic impurities or defects. As shown in Fig. 3, however, the line intensity [crudely $(A+B)\Delta H$] proves to be roughly independent of temperature. Such behavior is characteristic of the temperature-independent Pauli paramagnetism of a degenerate conduction-electron gas and constitutes the principal basis for concluding that the resonance is indeed due to *conduction* electrons. As will become clear, the line shape is affected by inhomogeneous crystal strain and does not, in general, provide an easily interpreted test of the mobile nature of the observed spins.

FIG. 4. The narrowest CESR spectrum thus far observed in In_2O_3. The platelet sample was prepared by flux-growth at 1475°K. The spectrum was taken at 77°K.

[10] N. Bloembergen, J. Appl. Phys. **23**, 1383 (1952).
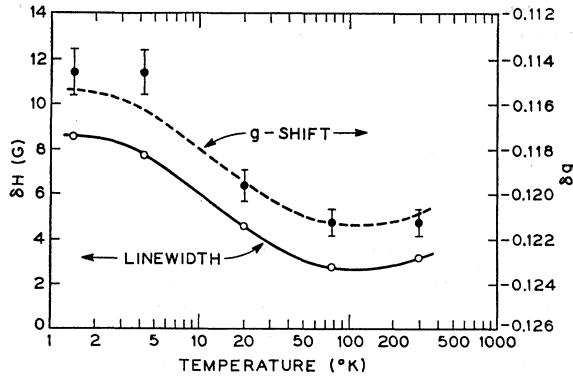[11] F. J. Dyson, Phys. Rev. **98**, 349 (1955).

FIG. 5. Temperature-dependent linewidth and g shift of the specimen of Fig. 4. The similarity of the two variations is emphasized by suitable choice of scales and by replotting the linewidth variation (solid curve) as the dashed curve on the δg points.

detectable. An increase in linewidth was visible (perhaps a factor of 2) but detailed studies of linewidth and line shape were not feasible. Further evidence of strain broadening is provided by our observation of irreversible increases in linewidth after temperature cycling or repeated remounting of a sample. Several specimens shattered in the course of such treatment, despite very gentle handling. Such fragility precluded any attempts to measure δg versus applied stress directly. Gross electrical conductivity variations of 10% or more were detected with a pair of mobile probes. It is, therefore, reasonable to conclude that these high concentration crystals contain defect-density fluctuations sufficiently large to produce appreciable strain gradients to which the g value is sensitive. Attempts to anneal the crystals at elevated temperatures produced little or no line narrowing though crystal *growth* at the highest possible temperature was beneficial, as noted earlier.

III. DISCUSSION

A. Line Shape and Width

The principal basis for attributing the observed resonance to conduction-electron spins is the essentially temperature-independent intensity. It is tempting to also invoke the fairly large asymmetry ratios found in sufficiently thick, cooled samples as further evidence of spin mobility, but this proves to be a more complicated matter. In the Dyson theory of CESR[11] the basic criterion for observation of asymmetry ratios greater than 2.7 is that the spin-lattice relaxation time T_1 be appreciably longer than the time T_D required for a spin to diffuse across the microwave skin depth δ. In our In_2O_3 samples we expect

$$T_D = 3\delta^2/2v_F^2\tau \simeq 6\times10^{-6} \text{ sec} \tag{1}$$

since $v_F \simeq 1.4\times10^7$ cm/sec for $n \simeq 10^{19}$ cm^{-3} and $m^*/m_e \simeq 0.55$ and $\tau \simeq 2\times10^{-14}$ sec. If the linewidth were entirely determined by $T_1 \sim 10^{-5}$ sec, it would be

$$\delta H \simeq 1.5/\gamma T_1 \simeq 8\times10^{-3} \text{ G}, \tag{2}$$

$(\gamma = g\beta/h \simeq 18.7$ Mc/G), whereas the measured linewidth ΔH is roughly three orders of magnitude larger. Since we have good reason to believe the line to be inhomogeneously broadened by crystal strains acting on the g value, this discrepancy is surprising only in its magnitude. However, it is far from clear what line shape we should expect under these circumstances $(T_1 \gtrsim T_D, \Delta H \gg \delta H)$.

Assuming that the observed absorption line is a superposition of homogeneous (lifetime-broadened) resonances of differing g values, let $G(H_0 - \bar{H}_0)$ represent the distribution of line-center positions, $H_0 = h\nu/g\beta$, relative to some mean value $\bar{H}_0$. The shape of the individual component lines is, in general, a complicated function of several parameters, as calculated by Dyson,[11] which we represent by the function $D(H - H_0)$ of width δH. We also assume that the homogeneous linewidth δH, presumed to arise from a true spin-lattice relaxation process, is much narrower than the width ΔH_0 of the line-center distribution function G (see Fig. 6). The resultant resonance takes the form

$$R(H - \bar{H}_0) = \int_{-\infty}^{\infty} D(H - H_0)G(H_0 - \bar{H}_0)dH_0. \tag{3}$$

The Dysonian line shape D may crudely be thought of as a sum of two terms, one symmetric about H_0 and the
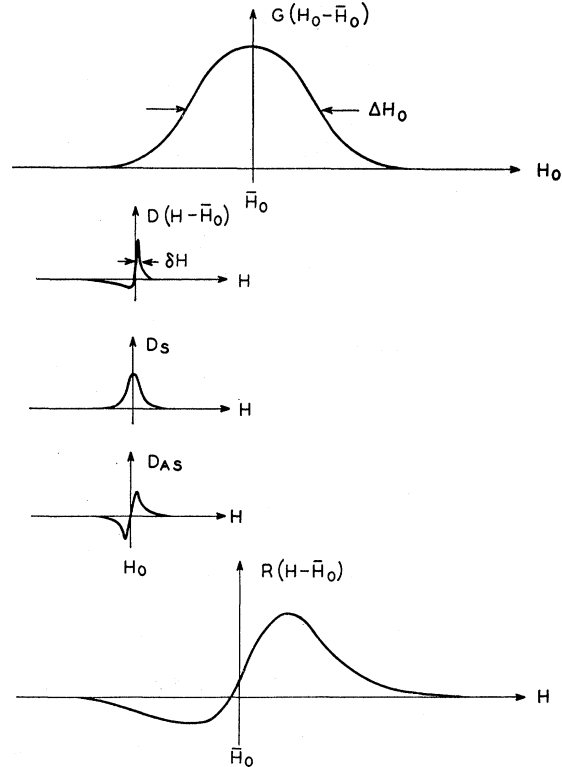

FIG. 6. Schematic representation of the absorption line shape expected for a distribution of component resonances whose shape may be described as a sum of symmetric and antisymmetric parts.

other antisymmetric:

$$D = aD_S + bD_{AS}, \qquad (4)$$

where the ratio of the coefficients a and b depends primarily on the ratio T_D/T_1 if the sample is electrically "thick." Roughly speaking, these coefficients correspond to the mixing of individual spin-resonance absorption and dispersion due to the varying microwave phase experienced by the diffusing spins. Since we assumed $\delta H \ll \Delta H_0$, the two components of D may be approximated using the Dirac δ function for simplicity:

$$D_S = \delta(H - H_0), \qquad (5a)$$

$$D_{AS} = -\frac{d\delta(H - H_0)}{dH} = \frac{d\delta(H - H_0)}{dH_0}. \qquad (5b)$$

The observed line R is now expressible as a weighted sum of the line-center function and its first derivative:

$$A(H - \bar{H}_0) = aG(H - \bar{H}_0) - b\frac{dG(H - \bar{H}_0)}{dH}. \qquad (6)$$

The steps of this approximate "folding" are illustrated in Fig. 6.

In practice we know neither the function G nor, a priori, the weighting coefficients a and b. It is, however, instructive to take D to be completely antisymmetric ($a = 0$, $T_D/T_1 \ll 1$) as a limiting case. Since the spread of g shifts is modest compared to the mean in our experiments ($\Delta H_0 < \bar{H}_0$), it is reasonable to assume G to be symmetric about $\bar{H}_0$. The complete antisymmetry of D is, of course, immediately reflected in $R = -dG/dH$. However, the line shape is the derivative of the distribution function and need not have any Dysonian character in detail. If, for example, we assume G to be a Gaussian distribution, the asymmetry parameter $A/B = (dR/dH)_{\text{max}+}/(dR/dH)_{\text{max}-} = 2.24$, which is less than the ratio expected for static but homogeneously broadened spins (a Lorentzian distribution is physically implausible and yields an even lower value, $A/B = 2$). A "tent-roof" distribution with relatively little curvature save at the peak appears to be required to yield A/B values much greater than 2. If the condition that G be symmetric about $\bar{H}_0$ is relaxed, arbitrary values of A/B may result. Finally, the precise degree of asymmetry of the component line shape D will also affect A/B by mixing dG/dH with d^2G/dH^2 in dR/dH.

Returning to the specific case of In_2O_3, it is now clear that little can be concluded from the shape of the inhomogeneously broadened resonance without prior knowledge of the line-center distribution function. The increased linewidth at low temperature reflects the increased range of the internal crystal strains. If the shape of the distribution has not been altered, one could conclude that the increased asymmetry results from an increase of b relative to a in Eq. (6). This would, in turn, be attributed to an increase in T_1 relative to T_D and,

since neither quantity is expected to be very temperature sensitive, would imply $T_D/T_1 \sim 0.4$, which is the value yielding greatest sensitivity of A/B on T_D/T_1.[9] All of this is speculation, however, due to our ignorance of G and its derivatives and their temperature dependence. Our most pessimistic estimate of T_1 must be distinctly longer than $T_2 \simeq 1.5/\gamma\Delta H \sim 3 \times 10^{-8}$ sec since the line is inhomogeneously broadened. The most optimistic value is somewhat longer than T_D. Thus we expect an unstrained sample would reveal 10^{-7} sec $< T_1 < 10^{-5}$ sec.

B. g Shift and Spin-Lattice Relaxation

Despite the intricacies of the preceding discussion one remarkable fact emerges: The spin-lattice relaxation time T_1 in In_2O_3 is between seven and nine orders of magnitude longer than the transport scattering time τ, yet the fractional g shift $g - g_0/g_0$ amounts to 6%. Such a large ratio of T_1/τ is surprising to an experimentalist familiar with CESR in metals since comparable degrees of decoupling between T_1 and τ are observed only in the lightest metals Li and Be, where the g shifts are extremely small ($\delta g/g_0 \gtrsim 10^{-5}$ for Li,[9] $\sim 5 \times 10^{-4}$ for Be).[9,12] In general as g shifts in metals increase, $\delta g/g \gtrsim 10^{-3}$, one must carefully purify and refrigerate the samples, thus attaining $\tau \sim 10^{-10}$ sec and $T_1 \sim 10^{-7}$-10^{-8} sec, i.e., a decoupling of only two to three powers of ten.

The situation in In_2O_3 is probably not at all unique, however. Müller and Schneider[13] have interpreted magnetic resonances which they and others have observed in several heavily doped or strongly illuminated n-type semiconductors as due to CESR of electrons in the conduction bands or in shallow donor bands. Their criteria, negative g shifts and absence of donor hyperfine interactions, are different from our own since the samples were apparently not degenerate. Their conclusions nevertheless seem reasonable and the results are similar to ours: CESR lines roughly 10 G in width are found with fractional g shifts of 2 to 10% at doping levels such that transport scattering times would be in the range 10^{-12}-10^{-14} sec. The significant observation to be made is that in every case where the nature of the conduction-band edge is known it is a single valley, as is believed to be true of indium sesquioxide.

For a nondegenerate band edge interacting with a p-like state, the calculations of Roth, Lax, and Zwerdling[14] predict the magnitude of the g shift:

$$\delta g \sim \frac{\lambda}{\Delta E}\left(\frac{m}{m^*} - 1\right), \qquad (7)$$

where λ is a spin-orbit coupling energy and ΔE is an energy-band splitting. Lacking any band-structure information on such an unlikely material as In_2O_3, it is

[12] J. E. Cousins and R. Dupree (unpublished).
[13] K. A. Müller and J. Schneider, Phys. Letters 4, 288 (1963).
[14] L. Roth, B. Lax, and S. Zwerdling, Phys. Rev. 114, 90 (1959).

only possible to say that the observed $\delta g = 0.12$ is not unreasonable since $\lambda \sim 0.4$ eV is appropriate to indium $5p$ states[15] and $\Delta E \sim 4$ eV is the magnitude of the direct gap found in optical studies.[5]

The spin-lattice relaxation time due to ionized, substitutional impurity scattering at a single-valley band edge has also been discussed by Elliott[14] and Yafet.[16] The relation between T_1 and τ is expected to take the form

$$T_1 \sim \tau / \delta g^2 c^{2/3}, \tag{8}$$

where c is the fractional concentration of scattering centers. Taking $c \sim 10^{-3}$ for In_2O_3 we obtain $T_1/\tau \sim 10^{-4}$, which is at least three orders of magnitude smaller than is found experimentally. Yafet[16] has pointed out that for a single-valley extremum at a point of high symmetry in

momentum space and for impurity sites having inversion symmetry Eq. (8) should be multiplied by an additional factor of $c^{-2/3}$. While the symmetry requirements are not fulfilled in In_2O_3 or the other II–VI compounds[13] such a factor would significantly reduce the discrepancy between theory and experiment. In view of the generality of the very large observed T_1/τ ratios the problem of ionized impurity scattering for single-valley band edges deserves more careful theoretical examination.

ACKNOWLEDGMENTS

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Na²³ Quadrupole Interaction in Ferroelectric Rochelle Salt*

N. C. Miller† AND P. A. Casabella‡

Interdisciplinary Materials Research Center, Rensselaer Polytechnic Institute, Troy, New York

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The first-order electric quadrupole splitting of the Na²³ nuclear magnetic resonance has been studied in single crystals of undeuterated Rochelle salt. At 30°C, in the upper paraelectric phase, the quadrupole coupling constants and asymmetry parameters for all four Na²³ sites were found to be the same: e^2Qq/h = 1.313 Mc/sec and $\eta = 0.809$. At 0°C in the ferroelectric phase, two coupling constants were measured, corresponding to the lower crystal symmetry. The values are $e^2Qq/h = 1.285$ Mc/sec with $\eta = 0.872$, and $e^2Qq/h = 1.407$ Mc/sec with $\eta = 0.675$. These results were analyzed according to the model of Blinc, Petkovsek, and Zupancic in which the changes are due to displacements of one hydroxyl ion and one water molecule. The data fit the model well and lend support to their view of the structural changes that take place when Rochelle salt becomes ferroelectric.

I. INTRODUCTION

THE macroscopic properties of Rochelle salt have been well known for a long time.[1–4] Rochelle salt (NaK tartrate tetrahydrate) has the unusual property that it is ferroelectric only between $-18°C$ and $+24°C$. The structure is orthorhombic, with symmetry $P2_12_12$

in both paraelectric phases.[5] The lattice undergoes a shear of $1'48''$ in the bc plane,[6] becoming monoclinic in the ferroelectric phase with symmetry $P2_1$ along a, the ferroelectric axis.[7–9] There are 4 molecules in the unit cell.

However, the structural problem has not been completed. The x-ray diffraction experiment of Beevers and Hughes was the first attempt to determine the structure

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